CHAPTER 6

THE CHEMISTRY OF CHLORINATION

6-1. HYPOCHLOROUS ACID (HOCL) FORMATION.

a. Swimming pool water is chlorinated for two important reasons:

(1) Disinfection: To kill bacteria and disease producing microorganisms.

(2) Oxidation: To react with and destroy and other contaminants such as algae, body oil, minerals, dust, and other materials which cause color, odor and turbidity.

b. To accomplish disinfection and oxidation, a chemical reaction between chlorine and water (hydrolysis) must occur to form hypochlorous acid (HOCL). Regardless of the chlorine source material used, the desired end product is hypochlorous acid, the chemical agent which destroys bacteria and other undesirable contaminants in pool water. Chlorination should occur after the water has left the equipment.

6-2. EFFECT OF pH.

Mixing chlorine and water does not necessarily produce hypochlorous acid. The pH of the water being treated determines whether the hydrolysis reaction produces an abundance of the desired hypochlorous acid or whether the primary product is hypochlorite ion (OCL), a relatively weak and ineffective oxidizing agent. At pH 7-2 approximately 60 percent of dissolved chlorine exists as hypochlorous acid. As pH values increase, the amount of HOCL decreases and the amount of hypochlorite ion increases. At pH 8-5, the dissolved chlorine exists as 90 percent OCL and only 10 percent HOCL. Thus, it can be seen that the disinfection and oxidation properties of chlorinated water are six times greater at pH 7-2 than at 8-5. For this reason, a pH of 7-8 is generally the upper limit for swimming pool water containing chlorine residual in the range of 0-5 to 1-0 parts per million (p/m). If pH is allowed to exceed this limit, the chlorine dosage must be increased in order to provide an adequate supply of hypochlorous acid.

6-3. OTHER REASONS FOR pH CONTROL.

In addition to its serious effect upon disinfection and oxidation, pH fluctuation must be avoided for other reasons. At high pH dissolved minerals such as iron and calcium precipitate, adding turbidity and increasing soil removal demand upon the filter system. High pH

in the presence of high total alkalinity contributes to scaling of filters, heaters, and piping. As pH drops below 7-0 the condition of the water becomes progressively acidic, producing eye irritation, corrosion, and other undesirable effects. Below 6-5 water becomes corrosive and damaging to metals in the recirculation system. pH ranges from 7-0 to 7-2 on the lower side and from 7-8 to 8-0 on the upper side are not objectionable, but they might well be thought of as safety zones to support the ideal range of 7-2 to 7-8.

6-4. FREE VS. COMBINED CHLORINE.

a. The potency of chlorine is affected by the ammonia content as well as the pH of the water. Ammonia is naturally present in virtually all surface waters and even more so in swimming pools since skin excretions and urinary discharges are ammonia sources. When dissolved chlorine exists predominantly as hypochlorous acid (HOCL) the residual is said to be "free available" chlorine . . . "free" to react with bacteria and other forms of soil. When chlorine reacts with ammonia the resulting compounds are called chloramines, and the chlorine becomes "combined" rather than "free" residual. Chloramines are undesirable because like hypochlorite ion (OCL), their oxidizing and germicidal power is greatly reduced.

b. The extent to which chlorine reactions produce chloramines rather than hypochlorous acid is governed largely by the amount of ammonia present. Chlorine prefers to chemically react with ammonia rather than with bacteria and soil. Thus, a large amount of ammonia in pool water causes the chlorine to exist largely as combined residual chloramine, greatly reducing the oxidation and disinfection activity.

6-5. SUPER CHLORINATION.

In the early history of swimming pool chlorination it was common practice to stabilize chlorine by adding ammonia to the water. The ammonia improved chlorine retention and prolonged the life of chlorine residual test readings, so it was reasoned that disinfection properties were enhanced by the method. Later studies, however, revealed the poor disinfection properties of chloramines. The practice has given way to a preference for burning out ammonia compounds through super chlorination (sometimes referred to as "breakpoint" chlorination).

6-6. BREAKPOINT CHLORINATION.

Breakpoint chlorination is accomplished by increasing chlorine dosage to a point at which all ammonia compounds in the water are completely oxidized and removed by chlorine reaction, after which point all dissolved chlorine exists as free available hypochlorous acid (HOCL) or hypochlorite ion (OCL). The amount of chlorine required to reach breakpoint depends upon the amount of ammonia present. Dosage instructions cannot therefore be expressed in pound or parts per million. An occasional super chlorination of 4 or 5 p/m in a typical pool will provide an acceptable means of assuring free residual chlorine.

6-7. INTENTIONAL CHLORINE STABILIZATION.

While the formation of chloramines in a swimming pool is considered objectionable, the stabilizing of chlorine with nitrogen compounds other than ammonia is considered desirable under some conditions. Such a practice may seem highly inconsistent with conclusions presented in the foregoing discussion, but the benefits to be derived become clear when the chemistry of chlorination is carefully studied.

6-8. STABILIZATION CHEMISTRY.

The hypochlorous acid molecule is highly desired for its oxidizing properties, but it is a highly unstable compound which rapidly dissipates in the presence of sunlight. This instability results in considerable chlorine waste, since free chlorine is rapidly destroyed even if it is not usefully consumed in reactions with bacteria and soil. Some degree of stabilization would therefore be desirable if such stabilization would slow the rate of chlorine dissipation without appreciably sacrificing oxidation and disinfection activity. Recently developed practices in swimming pool chlorination suggest that such stabilization can be accomplished satisfactorily with the use of cyanuric acid as the stabilizing agent. Chlorine reaction with cyanuric acid produces a relatively stable compound identified as chlorimide and, as in the case of chloramine formation, the dissolved chlorine exists predominately as combined residual. However, the chlorimide possesses significantly greater oxidation and disinfection properties than the chloramine group and is therefore an acceptable disinfection agent, whereas chloramine is not. Chlorimide reactions can also be produced with sulfamic acid and chlorinated chyantoins, but the use of these products is far less widespread than the chlorinated cyanurates.

6-9. STABILIZATION TECHNIQUE.

a. Laboratory and field studies of cyanuric chlorination technique suggest that, although the disinfection and oxidation properties of chlorimide are less than those of free hypochlorous acid, the loss can be at least partially offset by maintaining higher residuals of dissolved chlorine. It is generally believed that chlorine residuals in the presence of cyanuric acid should be maintained at 1-0 to 1-5 p/m, whereas 0-5 to 1-0 p/m is acceptable when free unstabilized chlorination technique is practiced.

b. The chlorinated cyanurates are used more commonly in private residential and small commercial pools at this writing. In larger swimming pools that are subject to heavy bathing loads, systems which provide free unstabilized chlorine residual are most frequently employed.

6-10. CONTROL OF pH AND CHLORINE RESIDUAL.

Oxidation and disinfection of swimming pool water can be accomplished only when adequate chlorine residual and proper pH values are maintained. The pool operator must therefore understand what factors cause pH fluctuation and chlorine dissipation and how to control those factors through proper chemical feeding practices.

6-11. CHLORINATION CONTROL.

a. Chlorine consumption and feed rates are easier to understand than pH control. As discussed previously, chlorine reacts with and destroys virtually all organic and inorganic compounds in pool water. In the process, the chlorine itself is destroyed and must be replaced. Therefore, the rate of feed is dependent upon the quantity of soil present in the water which, in turn, is largely dependent upon the bathing loads, bather preparation, weather, etc. It must also be remembered that free available chlorine dissipates even if it is not consumed by soil, so some chlorine feed is necessary even during periods when the pool is not in use.

b. Generally, knowledgeable technicians and public health personnel believe that free chlorine residual of not less than 0-5 p/m should be maintained at all times in the swimming pool. The better and safer practice is to feed at rates calculated to provide 1 p/m residual, with occasional super chlorination of 2 to 5 p/m, depending upon ammonia content and chlorine demand of the water.

6-12. CHLORINE TEST PROCEDURE (DPD METHOD).

The presence of chlorine is tested by use of a colorimetric test using N, N-diethyl-p-phenylenediainine (DPD) as a reagent chemical. The chlorine test procedure (DPD Method) is outlined in appendix C, Measurement of Residual Chlorine (DPD Method). The test is usually made periodically with the operator adjusting the chemical feed rates to compensate for the

rise or fall of the residual. The experienced operator learns to sense chlorine demand by observing bather loads, weather conditions, temperature, sunlight, and other influences. The periodic tests then are more often a confirmation of proper feed rates than a signal that rates need to he changed.

6-13. pH CONTROL.

a. The control of pH can be considerably more complicated than control of chlorine concentration. The chemistry of the pH factor itself is considerably more subtle than chlorine hydrolysis, and the factors which cause pH fluctuation are usually quite confusing to the nonchemist. However, the methods of control can be made reasonably clear. pH control begins with determining the pH of the water supply used initially to fill the pool and thereafter to make up water loss. Using the colorimetric test with phenol red reagent, the pH of the raw water is ascertained and then adjusted, if necessary, to the range of 7-2 to 7-8. Subsequent pH fluctuation is caused largely by the type of chlorine source used for oxidation and disinfection. Gas (elemental) chlorine, the most commonly used chlorine source in large swimming pools, decreases pH while the commonly used calcium hypochlorite and sodium hypochlorite sources tend to increase pH. Thus, if gas chlorination is practiced a substance must be fed concurrently to counteract the pH lowering effect of the gas chlorine. Soda ash, fed pound for pound with chlorine feed, is normally used for this purpose.

b. To counteract the pH elevating effects of sodium hypochlorite and calcium hypochlorite an acid counteractant must be used. Normally, pH control during hypochlorination is accomplished by feeding muriatic acid or solutions of sodium bisulphate.

c. The effect of chlorinated cyanurates upon pH has often been found to be very slight compared with gas chlorine and hypochlorites. Consequently, the pH is normally adjusted by occasional manual dosage of the counteractant rather than by feeding concurrently with the chlorine source.

6-14. pH EFFECT.

A number of other environmental conditions can affect the pH of swimming pool water; however, their enumeration would probably misplace the emphasis upon chlorination as the principal factor. For the most part, it is enough to say that when pH strays from the ideal zone of 7-2 to 7-8, regardless of cause, it should be promptly corrected. The operator must understand, however, that there are conditions under which the pH response to adjustment may be erratic and unpredictable. For example, a high pH of 9-0 might be adjusted to 7-8 by adding muriatic acid, only to ascend again to 9-0 within a few hours. Or, adding a small amount of corrective acid or alkali might produce a major response, sending the pH radically to an extreme high or low reading. Such reactions are attributable to the "total alkalinity" of the pool water and may indicate the need for corrections other than the addition of acid or soda ash. It is becoming common practice to equip swimming pools with testing equipment to measure both total alkalinity and pH, thus enabling the operator to make the necessary adjustments.

6-15. TOTAL ALKALINITY CONTROL.

a. Total alkalinity might be said to be a measure of the extent to which water is buffered or made to respond to pH adjustment. Water containing very low total alkalinity will respond radically to the addition of acid or alkali for pH correction, while water containing very high total alkalinity might respond very little.

b. Generally, swimming pool water should contain a minimum of 80 p/m and a maximum of 200 p/m total alkalinity. If the test procedure indicates a need for correction, it can usually be made by treating the water once, or for a short period of time, after which pH control is routinely accomplished by the methods discussed above. Total alkalinity that is too low can usually be corrected by adding a sufficient quantity of calcium carbonate ($CaCO_3$) to bring the level to 80 p/m. The corrective measure for total alkalinity that is too high may be somewhat more complicated. Essentially, undesirably high total alkalinity is corrected by adding muriatic acid. However, a single dose of a sufficient quantity to reduce the pH to 7-5 might not hold the pH at this desired level. The reading may consequently rise again within a few hours. When such a condition prevails, the acid dose must be repeated until the pH stabilizes at a desired level and total alkalinity is reduced to less than 100 p/m.